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<p>(21) International Application Number: PCT/NL97/00322</p> <p>(22) International Filing Date: 6 June 1997 (06.06.97)</p> <p>(30) Priority Data: 8/145712 7 June 1996 (07.06.96) JP</p> <p>(71) Applicants (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). JAPAN SYNTHETIC RUBBER CO., LTD. [JP/JP]; JSR Building, 2-11-24, Tsukiji, Chuo-ku, Tokyo 104 (JP).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): KOMIYA, Zen [JP/JP]; 2-18-33 M 1-3, Umezono, Tsukuba, Ibaraki 305 (JP). HIRAI, Tsuyoshi [JP/JP]; 2-13-28, Kawaguchi, Tsuchiura City 300 (JP). UKACHI, Takashi [JP/JP]; 5-22-9, Kamiya, Ushiku, Ibaraki 300-12 (JP).</p> <p>(74) Agent: DEN HARTOG, Jeroen, Hendrikus, Joseph; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).</p>		<p>(81) Designated States: AU, CA, CN, KR, US. European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With international search report.</p>
<p>(54) Title: LIQUID CURABLE RESIN COMPOSITION AND BUNDLED OPTICAL FIBERS</p> <p>(57) Abstract</p> <p>A liquid curable resin composition for coating optical fibers comprising (a) a urethane (meth)acrylate, (b) a polymerization initiator, and (c) polymer particles having an average particle diameter of 5 μm to 1mm. The composition exhibits excellent surface slip characteristics, superior curing characteristics, and sufficient strength, and is very useful as a material for manufacturing air-blown fiber cables.</p>		

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5 LIQUID CURABLE RESIN COMPOSITION AND
 BUNDLED OPTICAL FIBERS

 BACKGROUND OF THE INVENTION

10 Field of the Invention

 The present invention relates to a liquid curable resin composition for optical fibers exhibiting superior surface slip characteristics after cure, excellent curability, and superb durability, and to a
15 bundle of a plurality of optical fibers, having an outer layer of bundling resin exhibiting superior surface slip characteristics and superb durability.

Description of Related Art

 In the production of optical fibers, a resin
20 coating is provided for protection and reinforcement of molten glass fiber immediately after spinning. A known structure of the resin coating consists of a primary coating layer of a flexible resin which is applied to the surface of optical fiber and a secondary coating layer of
25 a rigid resin which is provided over the primary coating layer. A so-called optical fiber tape structural core is known in the art in the application of elemental optical fibers provided with resin coating. The optical fiber tape structural core is made from several such elemental
30 optical fibers, e.g. four or eight elemental optical fibers, by arranging these fibers in a plane and securing them with a binder to produce a tape structure with a rectangular cross section. A method for producing a multi-core structure by bundling two or more such optical
35 fiber tape structural cores is also known. For example, an eight-core structure is manufactured by covering two four-core optical fiber tape structures using a bundling

material. The resin composition for forming the primary coating is called a soft material; the resin composition for forming the secondary coating is called a hard material; the binder for preparing the optical fiber tape structural core from several elemental optical fiber is called a tape material; and the material for producing a multi-core structure by bundling two or more optical fiber tape structural cores is called a bundling material.

Air-blown fibers are also known. The air-blown fibers are made by bundling several optical fibers into a cylinder and blowing the bundled optical fibers into a pipe, installed in advance, using pressurized air. The bundling material used for this purpose is called an air-blown fiber bundling material.

In recent years, as integration of optical fiber cables has developed, an optical fiber cable containing a great number of optical fiber tape structural cores has been demanded. In addition, laying of air-blown fibers in remote locations is desired along with expansion of the area wherein optical fiber cables are used.

A resin used as the coating material for such optical fibers must have characteristics of being a liquid at ordinary temperatures with high processability; of providing good productivity at a high curing rate; of having sufficient strength and superior flexibility; of exhibiting very little physical change during temperature changes over a wide range; of having superior thermal resistance and superior resistance to hydrolysis; of showing superior long term reliability with little physical changes over time; of showing superior resistance to chemicals such as acids and alkalis; of exhibiting low moisture and water absorption; of exhibiting superior light resistance; of exhibiting high resistance to oils; and of producing little hydrogen gas which adversely

affects optical fiber characteristics.

In addition, excellent slip characteristics on the surface of the tape material and the bundling material are required for optical fiber tape structural cores used
5 in highly integrated optical fiber cables. Also, a bundling material exhibiting high slip characteristics at a pipe wall through which optical fibers are blown for manufacturing air-blown fiber is desired. In this manner, superior surface slip characteristics are required for the
10 tape material, bundling material, and air-blown fiber bundling material used in the manufacture of high integration optical fiber cables and air-blown fibers.

An object of the present invention therefore is to provide a liquid curable resin composition for coating
15 optical fibers satisfying the above-mentioned general requirements, exhibiting particularly superior surface slip characteristics after cure, a high curing rate, and a high strength, and suitable particularly for the manufacture of air-blown fibers.

20

SUMMARY OF THE INVENTION

These objects of the present invention are achieved in the present invention by the provision of a
25 liquid curable resin composition comprising (a) a urethane (meth)acrylate, (b) a polymerization initiator, and (c) polymer particles having an average particle diameter of 5 μm to 1 mm, and by a bundle comprising a plurality of coated glass optical fibers, the bundle having an outer
30 layer of cured bundling resin, the bundling resin comprising

- (a) a urethane (meth)acrylate
- (b) a polymerisation initiator and
- (c) polymer particles having an average particle size of

5 μm - 1 mm

DETAILED DESCRIPTION OF THE INVENTION
AND PREFERRED EMBODIMENTS

5

(a) Urethane (meth)acrylate

The urethane (meth)acrylate used in the present invention as the component (a) can be obtained by reacting a polyol, a diisocyanate, and a (meth)acrylate having a hydroxyl group, specifically, by reacting the isocyanate group of the diisocyanate with each of the hydroxyl groups of the polyol and the (meth)acrylate having a hydroxyl group.

The reaction can be carried out, for example, by the following methods: a method simultaneously reacting the polyol, the diisocyanate, and the (meth)acrylate having a hydroxyl group; a method reacting the polyol and the diisocyanate to obtain an intermediate, and reacting this intermediate with the (meth)acrylate having a hydroxyl group; a method of reacting the (meth)acrylate having a hydroxyl group and the diisocyanate, and then reacting the resulting compound with the polyol; a method of reacting the (meth)acrylate having a hydroxyl group and the diisocyanate, reacting the resulting compound with the polyol, then again reacting with the (meth)acrylate having a hydroxyl group.

Examples which can be given of the polyol used in these reactions include aliphatic, alicyclic, or aromatic polyether diols, polyester diols, polycarbonate diols, and polycaprolactone diols. These polyols may be used either individually or in combination of two or more. Random polymerization, block polymerization, or graft polymerization may be used for the polymerization of each structural unit in these polyols with no specific

limitations.

Given as specific examples of the aliphatic polyether diols are polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether diols obtained by the ring-opening copolymerization of two or more ionic-polymerizable cyclic compounds.

Examples of the ionic-polymerizable cyclic compounds include cyclic ethers such as ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide, 3,3-bischloromethyloxetane, tetrahydrofuran, 2-methyl-tetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorhydrine, glycidyl methacrylate, allyl glycidyl ether, allylglycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidyl benzoate.

Specific examples of the polyether diols obtained by the ring-opening copolymerization of two or more ionic-polymerizable cyclic compounds include binary copolymers obtained by the combination of tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydrofuran and 3-methyltetrahydrofuran, tetrahydrofuran and ethylene oxide, propylene oxide and ethylene oxide, butene-1 oxide and ethylene oxide; and ternary polymers obtained by the combination of, for example, tetrahydrofuran, butene-1-oxide and ethylene oxide.

It is also possible to use a polyether diol obtained by the ring-opening copolymerization of the above-mentioned ionic polymerizable compounds and a cyclic imine such as ethyl imine; a cyclic lactone such as

β -propiolactone or glycolic acid lactide; or a cyclic siloxane such as dimethylcyclopolsiloxane.

Examples of these polyether diols which are commercially available include PTMG650, PTMG1000, PTMG2000
5 (Mitsubishi Chemical Co., Ltd.); PPG400, PPG1000, EXCENOL
720, 1020, 2020 (Asahi Oline); "PEG1000, UNISAFE DC1100,
UNISAFE DC1800 (Nippon Oil and Fats Co., Ltd.); PPTG2000,
PPTG1000, PTG400, PTGL2000 (Hodogaya Chemical Co., Ltd.);
and Z-3001-4, Z-3001-5, PBG2000A, PBG2000B (Daiichi Kogyo
10 Seiyaku Co., Ltd.).

As examples of the alicyclic diols are an alkylene oxide addition diol to hydrogenated bisphenol A, an alkylene oxide addition diol to hydrogenated bisphenol F, and an alkylene oxide addition diol to 1,4-cyclohexane
15 dimethanol are given.

Further, given as examples of the aromatic polyether diols are an alkylene oxide addition diol to bisphenol A, alkylene oxide addition diol to bisphenol F, alkylene oxide addition diol to hydroquinone, alkylene
20 oxide addition diol to naphthohydroquinone, and alkylene oxide addition diol to anthrahydroquinone. These aromatic polyether diols are commercially available under the trademarks, for example, of Uniol DA400, DA700, DA1000, and DA4000 (Nippon Oil and Fats Co.).

25 Examples of the polyester diols include polyester diols obtained by the reaction of a polyhydric alcohol, and a polybasic acid. Given as examples of the polyhydric alcohols are ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol,
30 tetramethylene glycol, polytetramethylene glycol, 1,6-hexane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, 3-methyl-1,5-pentane diol, 1,9-nonane diol, and 2-methyl-1,8-octane diol. Given as examples of the polybasic acid are phthalic acid, isophthalic acid,

terephthalic acid, maleic acid, fumaric acid, adipic acid, and sebacic acid. Commercially available products of these polyester diols include, for example, Kurapole P-2010, PMIPA, PKA-A, PKA-A2, and PNA-2000 (Kuraray Co.).

5 Given as examples of the polycarbonate are polycarbonate of polytetrahydrofuran and polycarbonate of 1,6-hexane diol, and commercially available products, such as DN-980, DN-981, DN-982, DN-983 (Nihon Polyurethane), PC-8000 (PPG of the US), and PC-THF-CD (BASF).

10 Further, given as examples of the polycaprolactone diol are polycaprolactone diols obtained by the reaction of ϵ -caprolactone and a diol, such as ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol,
15 polytetramethylene glycol, 1,2-polybutylene glycol, 1,6-hexane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, and 1,4-butane diol. These polycaprolactone diols are also commercially available under trademarks such as PLACCEL 205, 205AL, 212, 212AL, 220, 220AL
20 (Daicell Co., Ltd.).

 Given as examples of polyols other than those mentioned above are ethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, hydrogenated
25 bisphenol A, hydrogenated bisphenol F, dimethylol compound of dicyclopentadiene, tricyclodecane dimethanol, pentacyclodecane dimethanol, β -methyl- δ -valerolactone, polybutadiene with terminal hydroxy groups, hydrogenated polybutadiene with terminal hydroxy groups, castor
30 oil-denatured diol, polydimethylsiloxane with terminal diols, and polydimethylsiloxane carbitol-denatured diols.

 The molecular weight, as measured with GPC (gel permeation chromatography) with the use of polystyrene standards, of the polyol used for producing the urethane

(meth)acrylate is usually 50 to 15,000, and preferably 100 to 8,000.

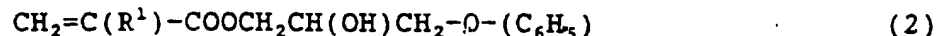
Given as examples of the diisocyanate used for producing the urethane (meth)acrylate in the present invention are 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, methylenebis(4-cyclohexyl)isocyanate, 2,2,4-trimethylhexamethylene diisocyanate, bis(2-isocyanate-ethyl)fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, lysine diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate, and tetramethylxylylene diisocyanate.

Among these diisocyanates, 2,4-tolylene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, and methylenebis(4-cyclohexylisocyanate) are particularly preferred.

These diisocyanates may be used either individually or in combination of two or more.

Examples of the (meth)acrylate having a hydroxyl group used for producing the urethane (meth)acrylate in the present invention include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxyalkyl(meth)acryloyl phosphate, 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate,

trimethylolpropane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, (meth)acrylates represented by the following structural formulas (1) or (2),



wherein R^1 is a hydrogen atom or a methyl group and n denotes an integer from 1 to 15. In addition, compounds obtained by an addition reaction between compounds

10 containing a glycidyl group, such as alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate, and (meth)acrylic acid can also be used.

Among these (meth)acrylates having a hydroxyl group, particularly desirable are 2-hydroxyethyl acrylate
15 and 2-hydroxypropyl acrylate.

These (meth)acrylates having a hydroxyl group may be used either individually or in combination of two or more.

The polyol, the diisocyanate, and the
20 (meth)acrylate containing a hydroxy group are used preferably in a proportion such that for one equivalent of the hydroxyl group of the polyol, 1.1 to 3 equivalents of the diisocyanate group contained in the diisocyanate compounds and 0.2 to 1.5 equivalents of the hydroxyl group
25 contained in the (meth)acrylate are used. It is desirable that the hydroxyl groups in the polyol and the (meth)acrylate be almost equivalent to the isocyanate groups in the diisocyanate compound.

It is possible to use a compound having a
30 functional group which can be added to an isocyanate group as an optional component in manufacturing the urethane (meth)acrylate. γ -mercaptopropyltrimethoxy silane and γ -aminopropyltrimethoxy silane are given as examples of the compound having such a functional group. Adhesion to

materials such as glass can be improved by using such a compound. These compounds can be used in an amount up to 10 parts by weight for 100 parts by weight of the total components for manufacturing the urethane (meth)acrylate.

5 Furthermore, in the case where the polyether diols are used as the polyol, a diamine may be added as an optional component. Ethylenediamine, tetramethylenediamine, hexamethylenediamine, para-phenylenediamine, 4,4'-diaminodiphenylmethane, and
10 polyether diamine are given as examples of such a diamine.

In addition to the above-mentioned urethane (meth)acrylate used as the component (a), the urethane (meth)acrylate obtained by the reaction of 1 mol of a diisocyanate and two mols of a (meth)acrylate containing a
15 hydroxy group can be used in the present invention. Such a urethane (meth)acrylate may be a reaction product of hydroxyethyl (meth)acrylate and 2,5- or 2,6-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, a reaction product of hydroxyethyl (meth)acrylate and and
20 2,4-tolylene diisocyanate, a reaction product of hydroxyethyl (meth)acrylate and isophorone diisocyanate, and a reaction product of hydroxypropyl (meth)acrylate and 2,4-tolylene diisocyanate. These urethane (meth)acrylate can be used in an amount of less than 30 parts by weight
25 for 100 parts by weight of the total amount of the urethane (meth)acrylates.

In the reaction for preparing the urethane (meth)acrylate (A), a urethanization catalyst such as copper naphthenate, cobalt naphthenate, zinc naphthenate,
30 n-butyl-tin-dilaurylate, triethylamine, 1,4-diazabicyclo[2.2.2]octane, or 2,6,7-trimethyl-1,4-diazabicyclo[2.2.2]octane is used, generally, in an amount of 0.01 to 1 part by weight for 100 parts by weight of the reaction raw materials. The

reaction temperature is normally in the range of 10 to 90°C, and preferably 30 to 80°C.

The urethane (meth)acrylate used in the present invention preferably has a weight average molecular weight as measured with GPC with the use of polystyrene standards, of 500 to 20,000. If the molecular weight is less than 500, this may cause a decrease in molecular weight between the cross-link points, resulting in cured products with insufficient flexibility and, occasionally, a large shrink stress when the composition is cured. If the molecular weight is larger than 20,000, the strength after cure may be insufficient.

The urethane (meth)acrylate is incorporated in the composition of the present invention in an amount preferably of 10 to 99 wt%, and particularly preferably 20 to 99 wt%.

(b) Polymerization initiator

The composition of the present invention is cured by heat and/or radiation. As the polymerization initiator (b) used in the present invention, a heat polymerization initiator or a radiation polymerization initiator can be used. Here, radiation means radiation from infrared light, visible light, ultraviolet light, X-rays, electron beams, α -rays, β -rays, and γ -rays.

A radical polymerization initiator such as a peroxide or an azo compound is usually used when the liquid curable resin composition is cured by heat. Given as specific examples of the radical polymerization initiator are benzoyl peroxide, t-butyloxybenzoate, and azobisisobutyronitrile.

When the composition of the present invention is cured with radiation, a radiation polymerization initiator is used. Examples of the radiation polymerization initiator include 1-hydroxycyclohexyl phenyl ketone,

2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, 5 Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanthone, diethylthioxanthone, 2-isopropylthioxanthone, 10 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one, 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide; and commercially available products, such as 15 Irgacure 184, 369, 651, 500, 907, CGI1700, CGI1750, CGI1850, CG24-61 (Ciba Geigy), Lucirin LR8728 (BASF), Darocure 1116, 1173 (Merck Co.), and Uvecryl P36 (UCB).

The above-described heat polymerization initiator may be used together with the radiation 20 polymerization initiator when the composition of the present invention is cured using both heat and radiation. The polymerization initiators are used preferably in an amount of 0.1 to 10 wt%, and particularly preferably 0.5 to 7 wt%, in the composition of the present invention.

25 (c) Polymer particles

Particles of polymers such as polyolefin, acrylic resin, polyurethane, polyamide, polystyrene, silicone resin, styrene/divinylbenzene copolymer are given as examples of the polymeric particles which are used as 30 component (c) in the composition of the present invention. Preferably, these resins are not fluorinated, as particles from fluorinated resins are very expensive, and tend to be incompatible with the urethane acrylate oligomer. These polymer particles may be either cross-linked polymer

particles or non-cross-linked polymer particles. The cross-linked polymer particles have an advantage in that the polymer particles are not mutually soluble with the resin solution and the form of the polymer particles is
5 hard to change. Particles of acrylic resin such as poly(methyl methacrylate) are particularly preferred as the polymer particles. Because of the absence of unsaturated bonds in the polymer main chain, acrylic resin has excellent weather resistance. In addition, since
10 acrylic resin can copolymerize with various cross-linking monomers in any optional proportion, highly cross-linked polymer particles can be obtained.

The polymer particles may be either particles produced by pulverizing a polymer or a polymer
15 manufactured in the form of particles, and may be either spherical or non-spherical. These polymer particles are commercially available under the trademarks of Mipelon XM-220 (manufactured by Mitsui Petrochemical Co., Ltd.), poly(methyl methacrylate) globular fine particles (MB and
20 MBX, manufactured by Sekisui Plastics Co., Ltd.), polystyrene particles (SBX, manufactured by Sikisui Plastics Co., Ltd.), high functional silicone powder (Torayfill, manufactured by Toray Dow Corning Co.), true globular functional fine particles polymer (Art Pearl,
25 manufactured by Negami Kogyo Co., Ltd.), and the like.

The specific gravity of the polymer particles is desirably the same or close to the specific gravity of the resin composition excluding the polymer particles (hereinafter referred to as "resin liquid").

30 Specifically, it is desirable that the difference between the specific gravity of the polymer particles and that of the resin liquid be in a range of between 0.3 to -0.3 g/ml. If the specific gravity of the polymer particles differs from that of the resin liquid markedly,

the polymer particles may precipitate or float in a short period of time when the viscosity of the resin liquid decreases at high temperatures, thereby impairing storage stability of the composition.

5 The average particle diameter of these polymer particles is preferably in the range of 5 μm to 1 mm, and particularly preferably 10 μm to 500 μm . If the average particle diameter of the polymer particle is less than 5 μm , the surface slip characteristics of the cured products
10 are insufficient; if more than 1 mm, it is difficult to disperse the polymer particles in the resin composition of the present invention in a stable manner.

In view of the requirements of ensuring superior coatability and surface slip characteristics by
15 maintaining the viscosity of the composition of the present invention in an appropriate range, the amount of polymer particles to be incorporated in the composition of the present invention should preferably be 0.1 to 30 wt%, and more preferably 0.5 to 20 wt%.

20 Other Components

Besides the above-described components, reactive diluents, other oligomers, non-particle polymer, and other additives may be incorporated to the composition of the present invention to the extent that the characteristics
25 of the composition are not adversely affected.

As the reactive diluent, monomers possessing a (meth)acryloyl group or a vinyl group other than the urethane (meth)acrylate of above-mentioned component (a) are used. Mono-functional monomers and poly-functional
30 monomers are given as such monomers.

The following compounds can be given as examples of the mono-functional monomer: alicyclic structure-containing (meth)acrylate, such as isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl

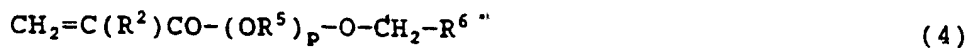
- (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, and cyclohexyl (meth)acrylate; (meth)acryloyl group-containing monomers, such as benzyl (meth)acrylate, 4-butylcyclohexyl
- 5 (meth)acrylate, (meth)acryloyl morpholine, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate,
- 10 isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, iso-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl
- 15 (meth)acrylate, iso-decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, iso-stearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol
- 20 (meth)acrylate, phenoxyethyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxy ethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, methoxy polyethylene glycol (meth)acrylate, methoxy polypropylene
- 25 glycol (meth)acrylate, diacetone (meth)acrylamide, isobutoxymethyl (meth)acrylamide, N-dimethyl (meth)acrylamide, t-octyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl (meth)acrylate,
- 30 N,N-diethyl (meth)acrylamide, N,N,N-dimethylaminopropyl (meth)acrylamide, compounds represented by the following formulas (3) to (5),



wherein R^2 is a hydrogen atom or a methyl group, R^3 is an

alkylene group having 2 to 6, preferably 2 to 4, carbon atoms, R^4 is a hydrogen atom or an alkyl group having 1 to 12, preferably 1 to 9, carbon atoms, and m is an integer from 1 to 12, preferably 1 to 8;

5



wherein R^2 has the same meaning as defined for formula (3), R^5 is an alkylene group having 2 to 8, preferably 2 to 5, carbon atoms; R^6 is a tetrahydrofuryl group, and p is an integer from 1 to 8, preferably 1 to 4; and

10



wherein R^2 , R^5 , and p have the same meanings as defined above, R^7 is a phenyl group, optionally substituted with one alkyl group having 1 to 12, preferably 1 to 9, carbon atoms; and vinyl group-containing monomers such as N-vinyl pyrrolidone, N-vinyl caprolactam, vinyl imidazole, vinyl pyridine, hydroxy butyl vinyl ether, lauryl vinyl ether, cetyl vinyl ether, 2-ethylhexyl vinyl ether, and N-vinyl carbazole.

20

As commercially available products of these mono-functional monomers, for example, Aronix M111, M113, M114, M117 (manufactured by Toagosei Chemical Industry Co., Ltd.); KAYARAD TC110S, R629, R644 (manufactured by Nippon Kayaku Co., Ltd.); and Viscoat 3700 (manufactured by Osaka Organic Chemical Industry, Ltd.) are given.

25

Among these compounds, isobornyl (meth)acrylate and N-vinylpyrrolidone are preferred.

30

The following compounds are given as examples of the poly-functional monomers: (meth)acryloyl group containing monomers, such as trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate,

ethylene glycol di(meth)acrylate, tetra ethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentylglycol di (meth)acrylate, 5 trimethylolpropane trioxyethyl (meth)acrylate, tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl) isocyanurate di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, di(meth)acrylate of alkylene oxide addition diol of 10 bisphenol A, di(meth)acrylate of alkylene oxide addition diol of hydrogenated bisphenol A, the epoxy (meth)acrylate made by adding (meth)acrylate to diglycidyl ether of bisphenol A; and vinyl group containing monomers such as triethylene glycol divinyl ether.

15 Given as commercially available products of these poly-functional monomers are Yupimer UV, SA1002, SA2007 (manufactured by Mitsubishi Chemical Co., Ltd.); Viscoat 700 (manufactured by Osaka Organic Chemical Industry, Ltd.); KAYARAD R-604, DPCA-20,-30,-60,-120, 20 HX-620, D-310, D-330 (manufactured by Nippon Kayaku Co., Ltd.); and Aronix M-210, M-215, M-315, M-325 (manufactured by Toagosei Chemical Industry Co., Ltd.). Of these poly-functional monomers, tricyclodecanedimethanol diacrylate and di(meth)acrylate of alkylene oxide addition 25 diol of bisphenol A are particularly preferred.

 These reactive diluents may be used either individually or in combination of two or more, and incorporated in the composition of the present invention in an amount of, usually 80 wt% or less, and preferably 20 30 to 70 wt%. The addition of the reactive diluents in this range ensures good coatability, an adequate curing rate, appropriate tenacity of cured products, and a low curing shrinkage.

 As other oligomers, polyester (meth)acrylate,

epoxy (meth)acrylate, polyamide (meth)acrylate, siloxane with a (meth)acryloyloxy group, fluorine-containing oligomer, silicon-containing oligomer, polysulfide oligomer, and the like can be given. In addition, given
5 as examples of non-particle polymers are reactive polymers obtained by the reaction of a copolymer of glycidyl (meth)acrylate and other vinyl group containing monomer and an acrylic acid; polyamide, polyamideimide, polyurethane, polybutadiene, polyether, polyester,
10 pentadiene derivatives, styrene-butadiene-styrene block copolymer, styrene-ethylene-butene-styrene block terpolymer, styrene-isoprene-styrene block copolymer, petroleum resin, xylene resin, and ketone resin.

Moreover, amines may be used in the composition
15 of the present invention to suppress generation of hydrogen gas which causes transmission loss in optical fibers. Diallylamine, diisopropylamine, diethylamine, diethylhexylamine, and the like are given as examples of such amines.

20 In addition to the above-mentioned components, various additives may be included in the composition of the present invention as required. Such additives include, for example, antioxidants, UV absorbers, photostabilizers, silane coupling agents, thermal
25 polymerization inhibitors, leveling agents, surfactants, preservatives, plasticizers, lubricants, coloring agents, solvents, fillers, aging preventives, wettability improvers, and coating surface improvers.

Here, given as examples of commercially
30 available additives are antioxidants, such as Irganox 1010, 1035, 1076, 1222 (manufactured by Ciba Geigy), Antigen P, 3C, FR, GA-80 (manufactured by Sumitomo Chemical Industries Co., Ltd.); UV absorbers, such as Tinuvin P, 234, 320, 326, 327, 328, 329, 213 (manufactured

- by Ciba Geigy), Seesorb 102, 103, 501, 202, 712, 704 (manufactured by Sypro Chemical Co.); and photostabilizers, such as Tinuvin 292, 144, 622LD (manufactured by Ciba Geigy), Sanol LS770 (manufactured by Sankyo Chemical Co.), Sumisorb TM-061 (manufactured by Sumitomo Chemical Industries Co., Ltd.). Given as examples of the silane coupling agents are γ -aminopropyltriethoxysilane, γ -mercaptopropyltrimethoxy-silane, and
- 10 γ -acryloxypropyltrimethoxysilane, and commercially available products, such as SH6062, 6030 (manufactured by Toray Silicone Co., Ltd.), and KBE903, 603, 403 (manufactured by Shin-Etsu Chemical Co., Ltd.).

- The viscosity of the composition of the present invention is usually in the range of 200 to 20,000 cps, and preferably 2,000 to 15,000 cps, measured at 25°C.
- 15

- The composition of the present inventions after curing has a slip value of no greater than about 3 kgf/mm², when tested as set forth herein. Preferably, the shear slip value of the cured composition is between about 0.1 and 2 kgf/mm².
- 20

EXAMPLES

- The present invention will be hereinafter described in more detail by way of examples which are given for illustration of the present invention and shall not to be construed as limiting the present invention.
- 25

Example 1

- 30 1,127 g of tricyclodecanedimethanol diacrylate, 1,453 g of 2,4-tolylene diisocyanate, 4.5 g of dibutyltin dilaurate, 1.5 g of 2,6-di-tert-butyl-4-methylphenol as a polymerization inhibitor, and 0.5 g of phenothiazine were placed in a reaction vessel equipped with a stirrer. The

mixture was cooled to 10°C over an ice-cooled bath and 1,266 g of hydroxyethyl acrylate was added while controlling the temperature at 20°C or lower. After the addition, the mixture was stirred for one hour at 10-20°C.

5 Then, 704 g of polyoxyethylene bisphenol-A ether and 2,250 g of polytetramethylene glycol having a number average molecular weight of 2,000 were added while controlling the temperature at 50°C or lower. The reaction was terminated after stirring for a further five hours at 50-60°C, thus

10 obtaining 6,806.5 g of a mixture of 83% urethane acrylate and 17% tricyclodecanedimethanol diacrylate.

To this product were added 493 g of a tricyclodecanedimethanol diacrylate, 773 g of isobornyl acrylate, and 700 g of ethoxylated bisphenol A diacrylate,

15 as reaction diluents, 895 g of N-vinylpyrrolidone, and 290 g of Irgacure 184(tm) (radiation polymerization initiator, manufactured by Ciba Geigy) and the mixture was stirred for three hours at 45-55°C. Then, 500 g of particles of cross-linked poly(methyl methacrylate) (Art Pearl

20 G-400(tm)), average diameter: 15 μ m, manufactured by Negami Kogyo Co. were added and the mixture was stirred for one hour at 20-30°C to obtain 10,457.5 g of the composition of the present invention.

25 Example 2

A composition of the present invention was prepared in the same manner as in Example 1, except that instead of 15 μ m particles, cross-linked poly(methyl (meth)acrylate) particles with an average diameter of 30 μ m, Art Pearl

30 G-200(tm), manufactured by Negami Kogyo Co. were used as polymer particles.

Example 3

A composition of the present invention was prepared

in the same manner as in Example 1, except for using polyurethane particles (average diameter: 15 μm , Art Pearl C-400(tm), manufactured by Negami Kogyo Co.) as polymer particles, instead of 15 μm cross-linked
5 poly(methylmethacrylate) particles.

Example 4

A composition of the present invention was prepared in the same manner as in Example 1, except that
10 polyurethane particles with an average diameter of 30 μm , Art Pearl C-200(tm), manufactured by Negami Kogyo Co.) were used as polymer particles, instead of 15 μm cross-linked poly(methylmethacrylate) particles.

15 Comparative Example

A composition was prepared in the same manner as in Example 1, except that no polymer particles were used.

Test Examples

20 The viscosity of the compositions prepared in Examples 1-4 and Comparative Example was measured, and the surface slip characteristics and the strength of the cured products were evaluated according to the following methods. The results are shown in Table 1.

25 <Measurement of viscosity>

The viscosity at 25°C was measured using a B-type viscometer manufactured by Tokyo Keiki Co., Ltd.

<Evaluation of surface slip characteristics of cured products>

30 1. Preparation of test specimens

The composition was applied to a glass plate using an applicator bar, to a thickness of 75 μm , followed by irradiation by UV light at 100 mJ/cm² in nitrogen atmosphere to provide a cured film with a thickness of 50

μm . The cured film was peeled from the glass plate and allowed to stand at 23° and 50% RH for 24 hours. This film was used in the test.

2. Shear slip test

- 5 A test specimen was attached to an aluminum sheet using a double-sided adhesive tape. Two sheets thus prepared were positioned so that the surfaces of the test specimens were in face to face contact and the sheets were fastened with a clip. The pressure at the surfaces of the test
- 10 specimens when fastened with a clip was 0.241 kg/mm². The two aluminum sheets were pulled apart at a pull-away speed of 50 mm/min to measure the force required for the sample sheets to slip.

<Evaluation of strength of the cured product>

15 1. Preparation of test specimens

- The composition was applied to a glass plate using an applicator bar to a thickness of 150 μm , followed by irradiation by UV light at 1.0 J/cm² in air to provide a cured film with a thickness of 120 μm . The cured film was
- 20 peeled from the glass plate and allowed to stand at 23°C and 50% RH for 24 hours. This film was used in the test.

2. Measurement of modulus of elasticity in tension

- A strip of the test leaf with a width of 6 mm was prepared to measure modulus of elasticity in tension at 23°C
- 25 according to JIS K7113. The tension at 2.5% stress was measured at a pulling rate of 1 mm/min to calculate the modulus of elasticity in tension.

	Example 1	Example 2	Example 3	Example 4	Compara. Example
Stress required for the sample to slip (kgf/mm ²)	1.01	0.59	1.38	0.63	4.83
5 Modulus of elasticity in tension (kg/cm ²)@23°C	87	96	86	93	96

10 Because of the excellent surface slip characteristics
after cure, the liquid curable resin composition for
coating optical fibers of the present invention is
particularly suitable as a taping material and a bundling
material used for high integration fiber cables and
15 air-blown fibers.

WHAT IS CLAIMED IS:

1. A liquid curable resin composition for covering optical fibers comprising:
 - 5 (a) a urethane (meth)acrylate,
 - (b) a polymerization initiator, and
 - (c) polymer particles having an average particle diameter of 5 μm to 1 mm.
2. The composition according to claim 1, wherein the
10 urethane (meth)acrylate (a) is obtained from a polyol, a diisocyanate, and a (meth)acrylate having a hydroxyl group.
3. The composition according to anyone of claims 1-2, wherein the urethane(meth)acrylate has a molecular
15 weight of 500-2000.
4. The composition according to anyone of claims 1-3, wherein the urethane(meth)acrylate is present in an amount of 20-99 wt.%.
5. The composition according to anyone of claims 1-4,
20 further comprising a reactive diluent in an amount of 20 to 70 wt%.
6. The composition according to anyone of claims 1-5, wherein the polymerization initiator is a radical polymerization initiator or radiation polymerization
25 initiator, or both.
7. The composition according to anyone of claims 1-6, wherein the polymer particles are acrylic resin particles.
8. The composition according to anyone of claims 1-7,
30 wherein the specific gravity of the polymer particles and that of the liquid curable resin is between 0.3 and -0.3.
9. The composition according to anyone of claims 1-8, wherein the polymer particles have an average particle

diameter of 10 μm - 500 μm .

10. The composition according to anyone of claims 1-9 wherein the polymer particles are present in an amount of 0.1-30 wt.%.
5
11. The composition according to anyone of claims 1-10, wherein the composition has a viscosity of 2,000 to 15,000 cp at 25°C.
12. The composition according to anyone of claims 1-11, wherein the amount of polymer particles is sufficient
10 so that said composition, after cure, has a shear slip of no greater than 3 kgf/mm².
13. The composition according to claim 12, wherein the amount of polymer particles is sufficient so that said composition after cure, has a shear slip of about 0.1-
15 2 kgf/mm².
14. A bundle comprising a plurality of coated glass optical fibers, the bundle having an outer layer of cured bundling resin, the bundling resin being a liquid curable resin according to any one of claims 1-
20 11.
15. A bundle according to claim 12 wherein the bundle has a substantial cylindrical form.
16. A bundle according to any one of claims 14-15 wherein the cured bundling resin has a shear slip of about 3
25 kgf/mm or less.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 97/00322

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C03C25/02 G02B6/44 C09D175/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C G02B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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